AFRL-AFOSR-UK-TR-2014-0016

Thermal Conductivity Designed Hard Protective Thin Films

Prof. Dr. Paul H. Mayrhofer

Technische Universitat Wien (Vienna University of Technology)
Materials Science and Technology
Karlsplatz 13
Wien (Vienna) 1040, AUSTRIA

EOARD Grant 13-2147

Report Date: May 2014

Final Report from 01 November 2012 to 31 October 2013

Distribution Statement A: Approved for public release distribution is unlimited.

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515, APO AE 09421-4515

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
23 May 2014	Final Report	1 November 2012 – 31 October 2013

4. TITLE AND SUBTITLE

Thermal Conductivity Designed Hard Protective Thin Films

5a. CONTRACT NUMBER

FA8655-13-1-2147

5b. GRANT NUMBER

Grant 13-2147

5c. PROGRAM ELEMENT NUMBER

61102F

6. AUTHOR(S)

Prof. Dr. Paul H. Mayrhofer

5d. PROJECT NUMBER

5d. TASK NUMBER

5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Technische Universitat Wien (Vienna University of Technology)
Materials Science and Technology
Karlsplatz 13
Wien (Vienna) 1040, AUSTRIA

8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
UNIT 4515
APO AE 09421-4515

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/AFOSR/IOE (EOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-AFOSR-UK-TR-2014-0016

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The main objective was to design hard coatings with directionally-dependent thermal transport properties. Coatings with layered arrangement of CrN and AlN layers were developed, as CrN typically has a thermal conductivity of ~2 W/mK whereas AlN can reach up to 300 W/mK at room temperature. This arrangement allows for high lateral thermal conductivity through the continuous AlN layers, and low thermal conductivity across the layers due to the periodic arrangement of the CrN layers. We have developed and studied various CrN/AlN layer combinations. The influence of the individual layer thickness was investigated by preparing multilayer coatings composed of 1-3 nm thin AlN layers and 1-10 nm CrN layers. Based on x-ray diffraction, transmission electron microscopy, and high resolution TEM, we can conclude that full stabilization of the AlN layers in their metastable cubic structure can be achieved up to layer thicknesses of 3 nm with the condition that the CrN layers need to be at least as thick as the AlN layers. Otherwise the AlN layers crystallize also in their stable ZnS (wurtzite type) structure. The superlattice coatings exhibit a characteristic hardness profile as a function of the bilayer period with a pronounced hardness maximum of 31 and 28 GPa. Highest thermal stability for these superlattice coatings is obtained when the columnar growth is inhibited. Based on our study we can conclude that a knowledge-based combination—which is derived from this project—of CrN and AlN layers leads to outstanding mechanical properties as well as thermal stability.

15. SUBJECT TERMS

EOARD, nanocoatings, protective coatings, hard materials, superlattices, CrN, AlN

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18, NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Lt Col Randall Pollak
UNCLAS	UNCLAS	UNCLAS	SAR	10	19b. TELEPHONE NUMBER *(Include area code)* +44 1895 616115, DSN 314-235-6115

Report for the

EOARD Grant/Award FA8655-13-1-2147

about

Thermal Conductivity Designed Hard Protective Thin Films

by

Univ.-Prof. Dr. Paul H. Mayrhofer
Materials Science and Technology
Vienna University of Technology

Vienna, May 2014

Contents

1 Abstract

The main objective of the proposed research work was to design coatings to allow for different thermal transport in lateral as well as perpendicular direction and to understand the mechanisms behind the directional dependent thermal management. Therefore, we developed coatings composed of a layered arrangement of CrN and AlN layers, as CrN typically has a thermal conductivity of ~2 W/mK whereas AlN can reach up to 300 W/mK at room temperature. This layered arrangement allows for high lateral thermal conductivity through the continuous AlN layers, and low thermal conductivity across the layers due to the periodic arrangement of the low thermal conductivity CrN layers. We have developed and studied various CrN/AlN layer combinations.

The influence of the individual layer thickness is investigated by preparing multilayer coatings composed of 1, 2, and 3 nm thin AlN layers and CrN layers with thicknesses ranging from 1 to 10 nm. Based on X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) we can conclude that a fully stabilization of the AlN layers in their metastable cubic structure can be achieved up to layer thicknesses of 3 nm with the condition that the CrN layers need to be at least as thick as the AlN layers. Otherwise the AlN layers crystallize also in their stable ZnS wurtzite type structure. The superlattice coatings exhibit a characteristic hardness profile as a function of the bilayer period Λ with a pronounced hardness maximum of 31 and 28 GPa. Highest thermal stability for these superlattice coatings is obtained when the columnar growth is inhibited. The study initiated a deep collaboration with the Air Force Research Laboratory in Dayton, Ohio, where currently selected samples (out of this project) are investigated based on their thermal conductivity.

Based on our study we can conclude that a knowledge-based combination—which is derived from this project—of CrN and AlN layers leads to outstanding mechanical properties as well as thermal stability.

2 Report on the EOARD grant

This section briefly summarizes the main results obtained during the EOARD Grant/Award. A summary of how the grant was used to obtain the proposed goals of the project is given. For information, the goals, the workplan and dissemination plan of the original proposal are added in the following chapters.

2.1 Objective of the proposal

The main objective of the proposed research work is to design coatings to allow for different thermal transport in lateral as well as perpendicular direction and to understand the mechanisms behind the directional dependent thermal management. **The strategy is to develop multilayer coatings combining $Cr_{1-x}Al_xN$ layers with different composition and structure. Hence, in the extreme cases c-CrN/c-AlN or c-CrN/w-AlN multilayers (c: face centered cubic; w: hexagonal wurtzite structure) will be developed.** In addition to the industrial relevance, the combination of CrN-rich and AlN-rich layers to form a multilayer arrangement are chosen based on the possibility to have a 100 times larger thermal conductivity in one phase (w-AlN with 285 W/mK at 300 K [1] and c-AlN with 250-600 W/mK [2]) than the other (CrN with 2 W/mK at room temperature, RT [3]).

A topic, which is important for many different areas like machining industry, automotive, energy- and aerospace industry, is to obtain coatings with excellent mechanical and thermal

properties [4]. $Cr_{1-x}Al_xN$ films and/or their alloys are in favor for such applications due to their excellent physical, chemical, and mechanical properties (like high hardness, good abrasive and sliding wear resistance, and high oxidation and corrosion resistance) [5-13]. **The thermal properties (especially thermal conductivity) of this important class of materials but especially the design to obtain directional dependent thermal properties have received much less attention. Consequently, this is the main focus of this project.**

As a result of this project, new data on the design concept of various protective coatings to guarantee for individual (thermal) properties in various directions (in-plane or out-of-plane) will be obtained. It is expected that these multifunctional coatings can expand functionality and reliability of machining, automotive, energy- and aerospace systems.

1. G.A. Slack, R.A. Tanzilli, R.O. Pohl, J.W. Vandersande, J. Phys. Chem. Solids 48, 7 (1987), 641-7
2. J. Wang, W.L. Wang, P.D. Ding, Y.X. Yang, L. Fang, J. Esteve, M.C. Polo, G. Sanchez, Diamond Relat. Mater. 8 (1999) 1342
3. M.K. Samani, G.C.K. Chen, X.Z. Ding, X.T. Zeng, Key Eng. Mat. 447-448, (2010) 705-9
4. P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens, Prog. Mater. Sci. 51 (2006) 1032
5. O. Knotek, F. Löffler, and H.-J. Scholl, Surf. Coat. Technol. 45 (1991) 53.
6. J.C. Sánchez-López, D. Martínez-Martínez, C. López-Cartes, A. Fernández. M. Brizuela, A. García-Luis, and J.I. Oñate, J. Vac. Sci. Technol. A 23 (2005) 681.
7. A. Sugishima, H. Kajioka, and Y. Makino, Surf. Coat. Technol. 97 (1997) 590.
8. Y. Makino and K. Nogi, Surf. Coat. Technol. 98 (1998) 1008.
9. B.C. Schramm, H. Scheerer, H. Hoche, E. Broszeit, E. Abele, and C. Berger, Surf. Coat. Technol. 188 (2004) 623.
10. M. Kawata, A. Kimura, and T. Suzuki, J. Vac. Sci. Technol. A 20 (2002) 569.
11. E. Lugscheider, K. Bobzin, St. Bärwulf, and Th. Hornig, Surf. Coat. Technol. 133 (2000) 540.
12. H. Willmann, P.H. Mayrhofer, P.O.Å. Persson, A.E. Reiter, L. Hultman, and C. Mitterer, Scripta Mat. 54 (2006) 1847.
13. A.E. Reiter, V.H. Derflinger, B. Hanselmann, T. Bachmann, and B. Sartory, Surf. Coat. Technol. 200 (2005) 2114.
14. R.M. Costescu, D.G. Cahill, F.H. Fabreguette, Z.A. Sechrist, S.M. George, Science 303 (2004) 989-90
15. J. Lin, J.J. Moore, B. Mishra, M. Pinkas, W.D. Sproul, Surf. Coat. Technol. 204 (2009) 936-40.
16. J.-K. Park, Y.-J. Baik, Surf. Coat. Technol. 200 (2005) 1519-23.
17. S.-K. Tien, J.-G. Duh, Thin Solid Films 494 (2006) 173-8.
18. S. Inoue, F. Okada, K. Koterazawa, Vacuum 66 (2002) 227-31.
19. P.H. Mayrhofer, G. Tischler, C. Mitterer, Surf. Coat. Technol. 142 (2001) 78-84.
20. H. Willmann, P.H. Mayrhofer, L. Hultman, C. Mitterer, Int. Heat Treatm. Surf. Engin. 1 (2007) 75-79

2.2 Goals of the proposal

Development of CrN/AlN multilayer and superlattice coatings where the AlN layers are either stabilized in their metastable cubic structure or crystallize in their stable hexagonal wurtzite-type structure w-AlN.

2.3 Main results of the project

Within the framework of this Award one paper has been published, highlighting the major result [1]. Important to mention is that also based on the international cooperation with the Air Force Research Lab in Dayton/OH, that started due to this AWARD, further work on developed coatings is in progress. Samples are already on the way to Dayton for detailed investigation of the thermal conductivity of various coating architectures of the CrN/AlN multilayers and superlattice coatings.

A short summary and an overview of the major findings will be presented in the following chapters.

2.3.1 Summary

Ceramic-like coatings are widely used for various industrial applications because of their outstanding properties like high thermal stability, oxidation resistance and abrasion resistance. Particularly, transition metal nitrides, such as CrN are well known and investigated with respect to their microstructure, morphology, thermal and mechanical properties. Due to the demand of versatile requirements smart architectural designs such as nanocomposite and multilayers become more important during the last decades.

Based on some difficulties to accurately obtain the thermal conductivity of the samples, we first concentrated on the development of various CrN/AlN multilayer coatings with respect to their structural, mechanical and thermal properties. The influence of the individual layer thickness is investigated by preparing multilayer coatings composed of 1, 2 and 3 nm thin AlN layers and CrN layers with thicknesses ranging from 1 to 10 nm. Based on X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) it can be concluded that a fully stabilization of the AlN layers in their metastable cubic structure can be achieved up to layer thicknesses of 3 nm with the condition that the CrN layers need to be at least as thick as the AlN layers. Otherwise the AlN layers crystallize also in their stable ZnS wurtzite type structure. The superlattice coatings exhibit a characteristic hardness profile as a function of the bilayer period Λ with a pronounced hardness maximum of 31 and 28 GPa. Moreover, mixed cubic/wurtzite structured AlN layers leads to interrupted grain growth and wide columnar structure. **These coatings indicate highest thermal stability** as they provide less grain boundaries and consequently less diffusion paths.

Continuous lattice fringes throughout the alternating CrN and AlN layers can clearly be seen in HR-TEM investigations, see for example Figs. 1a and b. The Fast Fourier Transformation (FFT) of the AlN layers confirms their cubic structure, inset in Fig. 1b. Thicker AlN layers tend to crystallize in their stable wurtzite structure, as the coherency strains to the CrN layers are too weak for a fully cubic stabilization, Figs. 1c and d. But even if both layer types (CrN and AlN) are just cubic, their hardness strongly depends on the layer thickness ratio. This can easily be obtained from Fig. 1e when comparing the superlattice coatings with 1 and 2 nm thin AlN layers having a bilayer period of ~5.5 nm. While the coatings with 2 nm thin AlN layers exhibit a hardness maximum (H ~31 GPa) the coatings with 1 nm AlN passed already the peak-hardness.

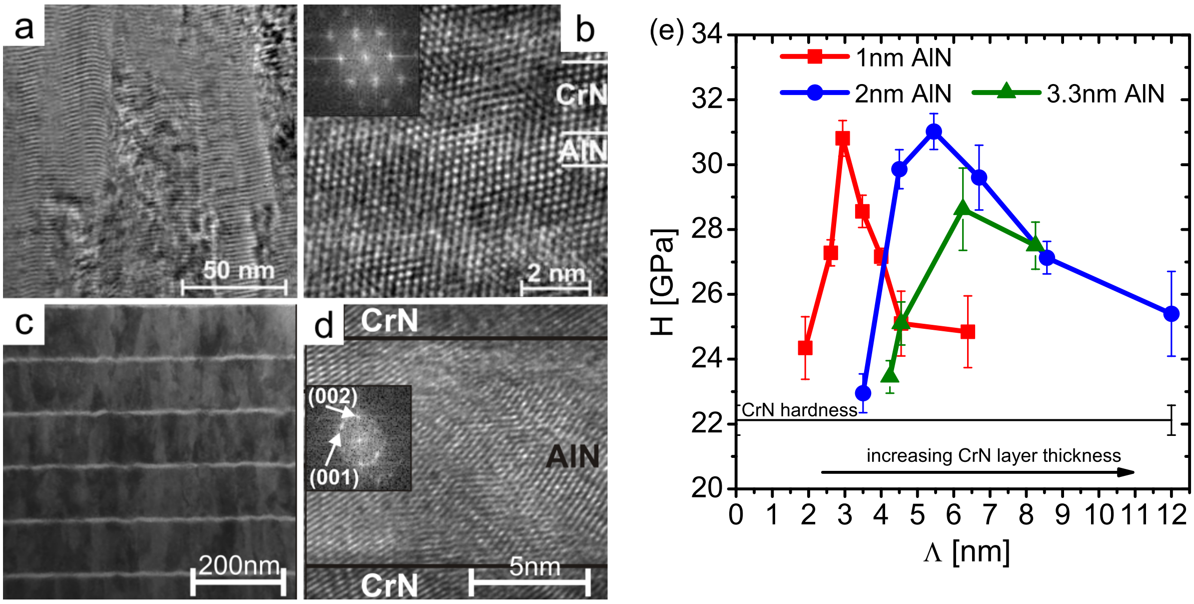

Fig. 1 Cross-sectional TEM and HR-TEM images of CrN/AlN coatings with ~1 nm thin AlN layers (a and b) and ~10 nm thin AlN layers (c and d). The inset in (b) and (c) is the corresponding FFT of the AlN layer [1]. (e) Hardness of CrN/AlN superlattice coatings as a function of the bilayer period Λ and the AlN layer thickness.

By optimizing the CrN/AlN layer thickness ratios to 2/1, 3.5/2, and 3/3 nm highest as-deposited hardnesses of ~31 GPa can be obtained. Unfortunately, this is combined with a low thermal stability, whereas **coatings with CrN/AlN layer thickness ratios below 1 (i.e., thinner CrN than AlN layers) are able to remain their as-deposited hardnesses of ~24 GPa even after annealing at 1100 °C.** Complementary differential scanning calorimetry and structural investigations after various annealing steps by transmission electron microscopy and X-ray diffraction show, that for these coatings the properties are mainly determined by the higher overall content of AlN. Contrary, for CrN/AlN layer thickness ratios above 1, the thermal stability is mainly determined by the dissociation of the CrN layers to Cr and N_2 via the formation of Cr_2N. Our results clearly show that especially for CrN/AlN superlattices higher as-deposited hardnesses are balanced with lower thermal stability.

1. M. Schlögl, B. Mayer, J. Paulitsch, P.H. Mayrhofer, Thin Solid Films 545 (2013) 375.

2.3.2 Overview on "Thermal stability of CrN/AlN superlattice coatings" [2.7.1]

The thermal stability and the thermo-mechanical properties of CrN/AlN superlattices composed of 1, 2, or 3 nm thin AlN layers combined with different CrN layer thicknesses were studied. HRTEM investigations of as-deposited coatings indicate large columnar grains elongated in the growth direction throughout the individual AlN and CrN layers for CrN/AlN layer thickness ratios above 1. For these coatings the AlN layers are fully stabilized in their metastable cubic structure by coherency to the cubic CrN layers. Coatings having CrN/AlN layer thickness ratios below 1 (1.5/2 and 1/3) are characterized by the coexistence of cubic and wurtzite phases. Here, the AlN layers are not fully stabilized in their metastable cubic structure by the cubic structured CrN layers, and therefore crystallize also in their stable wurtzite structure. This leads to a discontinuance of the columnar growth, and hence shorter columns, and a more equiaxed growth morphology. Especially these superlattices exhibit the highest thermal

stability as they exhibit no pronounced column boundaries, which are usually fast diffusion pathways. Even after annealing at 1100 °C the hardness is at their as-deposited value of ~21 GPa, as the dissociation of the CrN layers towards Cr via Cr_2N is effectively retarded by the AlN layers. Furthermore, the mechanical properties of these coatings are supported by the high AlN phase fraction upon annealing. The superlattice with CrN/AlN layer thickness ratios above 1 (2/1 and 3.5/2), having high as-deposited hardness values of ~31 GPa, rapidly soften upon annealing. Already for T_a = 1100 °C the hardness is reduced to 6.6 and 10.8 GPa, as their CrN layers are already fully decomposed to Cr. For these coatings the AlN layers are not able to retard the CrN dissociation and to support the overall coating behavior.

Based on our studies we can conclude that superior properties in the as-deposited state do not guarantee for superior thermo-mechanical behavior.

2.4 International cooperation

The following cooperation were established and deepened within the described project, to strengthen and increase the scientific network, success and output. Furthermore, the cooperation help to successfully use the funding with high output.

- **Air Force Research Laboratory (AFRL), Dayton, Ohio, USA:** *Dr. Andrey Voevodin*.

2.5 Unexpected results, success and obstacles

The most unexpected result is, that even when the AlN layers are not stabilized in their cubic structure, but combined with around 1 nm thin cubic CrN layers, the overall coating hardness is relatively high with 25 GPa. Especially this coating exhibits also the highest thermal stability, and even after annealing at 1100 °C, the hardness is nearly unchanged at 25 GPa.

As a major obstacle the detailed characterization of the thermal conductivity can be named. After several unsuccessful investigations and Lithographic Preparation for 3-omega thermal conductivity measurements, we started the collaboration with the air force research lab in Dayton, Ohio, see chapter above.

2.6 Declared costs within the project

The major costs where the salary of one Post Doc, for developing and investigation of coating materials. Additional costs are due to consumables for coating development, like substrates (silicon), targets (aluminum and chromium), and investigation by X-ray diffraction and transmission electron microscopy.

2.7 Appendix; Dissemination with in the project

2.7.1 Papers

1. M. Schlögl, J. Paulitsch, P.H. Mayrhofer, *Thermal stability of CrN/AlN superlattice coatings*, Surface and Coatings Technology 240 (2014) 250.

2.7.2 Presentations

Invited oral presentations at scientific conferences

1. **P.H. Mayrhofer,** Innovative Ceramic-Like Coatings for Tooling, Machining, Aerospace, Energy and Automotive Industry, 37th International Conference and Exposition on Advanced Ceramics and Composites, Jan. 27–Feb. 1, 2013, Daytona Beach (USA).

2. **P.H. Mayrhofer,** Innovative Hard Coatings for Machining and Wear Protection through Age Hardening and Improved Oxidation Resistance, Euro PM2013 Congress & Exhibition, Sep. 15–18, 2013, Gothenburg (SE).

Contributed oral presentations at scientific conferences

3. M. Schlögl, B. Mayer, J. Paulitsch, J. Keckes, C. Kirchlechner, **P.H. Mayrhofer**, Mechanical properties, fracture toughness, and thermal stability of CrN/AlN superlattice and multilayer thin films, AVS 59th International Symposium, Oct. 28–Nov. 2, 2012, Tampa, FL (USA).

3 CV of Paul H. Mayrhofer

Paul Mayrhofer studied Materials Science at the University of Leoben. After his PhD in 2001 on Materials Science Aspects of Nanocrystalline PVD Hard Coatings in collaboration with the West Bohemian University in Plzen, CZ, he worked as University Assistant at the University of Leoben and Post-Doc at the Center for Microanalysis of Materials and the University of Illinois at Urbana-Champaign, USA. He habilitated in 2005 with the topic Nanostructural Design of Hard Thin Films at the University of Leoben. He spent his Erwin-Schrödinger-Fellowship in the years 2005 and 2006 as a Researcher at Materials Chemistry, RTWH Aachen, and Thin Film Physics Division, Linkoping University. Paul Mayrhofer was Key Researcher form 2007 to 2009 and Associate Professor of Nanostructured Materials from 2010 at the University of Leoben. In 2012 he has been appointed Full Professor of Materials Science at the Vienna University of Technology. His research activities focus on the development and characterization of vapor phase deposited nanostructured materials by a combination of computational and experimental material science. **161 publications** (130 in SCI listed Journals with around 2200 citations without self-citation to these, including 2 invited publications, 8 book chapters, and 23 articles in proceedings), an h-index of 29 (without self-citation 24), and **36 invited talks (incl. 5 keynote and 3 plenary) at international conferences**.

PERSONAL INFORMATION

THIS SECTION REMOVED FOR PUBLIC DISTRIBUTION VERSION.